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14. ABSTRACT
Room temperature quantum efficiencies of 2 micron thick Ag/n-Si composite films as a function of electric field were calculated for incident wavelengths of 3, 5, 8 and 14 microns, representing the first time such a calculation was made for a metal-semiconductor composite. With energies less than the Ag-Si Schottky barrier height, the signal current is carried by electrons tunneling through the barrier, for composites with Ag nanoparticles 5nm in size in an applied electric field of 2x10e+6 V/cm, the quantum efficiencies are between 10% and 35% depending on the incident wavelength. They increase rapidly with electric field and asymptotically a large fraction of the radiation absorbed in the Ag particles.

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Electric field dependence of quantum efficiencies of Ag/n-Si composites in the infrared at room temperature

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Room temperature quantum efficiencies of Ag/n-Si composite films as a function of electric field are calculated for incident radiation wavelengths of 3, 5, 8 and 14μm using a previously derived formula. With energies smaller than the Ag-Si Schottky barrier height, the signal current is carried by electrons tunneling through the barrier. For composites with Ag particle sizes of 5nm, in an applied electric of $2x10^6$ volts/cm, the quantum efficiencies are between 10 and 35%, depending upon the wavelength. They increase rapidly with electric field and asymptotically approach a large fraction of the absorbed incident radiation in the Ag particles.

An expression was previously derived for the quantum efficiency of Schottky barrier metal-semiconductor composite photon detectors as

$$\eta(\upsilon) = \acute{\eta}(\upsilon)P_{esp}(E)P_t(E)/\{1 - [1 - P_{esp}(E)]\acute{P}_t(E)\}^1. \qquad (1)$$

In these detectors metal particles, nanometers in size, are embedded in a semiconductor matrix. Photons at frequency υ are absorbed in the metal particles producing free photoexcited electrons, which cross the metal-semiconductor interface into the semiconductor conduction band, giving rise to a signal current. Examples of such buried Schottky barrier detectors for sensing at 1µm are $CoSi_2$ particles 10nm in size and larger in p-type silicon[2] and 3nm As precipitates in undoped GaAs[3]. The quantum efficiency of the former at liquid nitrogen temperature (LNT) of 1.3%, was approximately six times higher than the corresponding planar structure. The latter had a room temperature quantum efficiency of 2-2.5%. For detecting radiation in the 8 - 14µm range, Ag nanoparticles in $CuInSe_2$ were used [4]. The device had a voltage responsivity of 10^2 volts/watt at LNT with a $D^* = 10^6$cm $Hz^{1/2}W^{-1}$. As modest as these values may appear, the composite film was only 500nm thick. The enhanced sensitivities these buried Schottky barriers have over their planar counterparts come from increased surface areas and geometrical factors, producing measured increases of an order of magnitude[1,5]. Films used here had Ag particles, treated as spherical in shape, embedded in an n-type silicon matrix (Ag/n-Si). Unlike the composites above, this study involved incident radiant energies smaller than the Ag-Si Schottky barrier.

$\acute{\eta}(\upsilon)$ is the fraction of incident flux at frequency υ that is absorbed in the Ag particles, and the remaining portion is the probability for a photoexcited electron to escape from a spherical Ag particle. This latter expression, derived in an earlier publication[5], contains three terms. $P_{esp}(E)$ is the probability that a photoexcited electron hits the inner boundary of the Ag particle with energy E and escapes. $\acute{P}_t(E)$ is the probability that an electron can survive any inelastic scattering between reflections averaged throughout a sphere. $P_t(E)$ is the average probability for a photoexcited electron at **r** in a spherical particle centered at r = 0 to reach the particle boundary without inelastic scattering. $\acute{P}_t(E)$ and $P_t(E)$ are given by[5]

$$\acute{P}_t(E) = l/2R[1 - \exp(-2R/l)] \qquad (2)$$

$$P_t(E) = 3/2(l/R)^4\{2(R/l) - 3 + \exp(-2R/l)[2(R/l)^2 + 4(R/l) + 3]\}. \qquad (3)$$

R is the radius of the spherical Ag particle and $l(E)$ is the mean free path of the electron in the particle at energy E. If a photoexcited electron with kinetic energy E greater than the Ag-Si Schottky barrier height hits the inner boundary of the Ag at such an angle that the perpendicular kinetic energy is still greater than this height and can thus escape, then $P_{esp}(E)$ is given by[5]

$$P_{esp}(E) = \tfrac{1}{2}[1 - (\Phi/E)^{1/2}] \qquad (4)$$

where Φ is the measured Ag-Si Schottky barrier height of 0.6 eV [6]. If however, the kinetic energy E is smaller than 0.6eV then this expression must be replaced with the transmission probability for electrons to tunnel through the barrier.

Figure 1 shows an energy band diagram at the interface between a Ag particle and the Si matrix. This is the usual triangular approximation for the energy band diagram as a function of distance for this interface and the transmission probability for this barrier is given by [7]

$$T\left(E_{avg\perp}\right) = exp\left(-\frac{4}{3}\frac{\sqrt{2m^*}}{\hbar q}\frac{W^{3/2}}{E_{field}}\right) \quad , \qquad (5)$$

where $\hbar$ is Planck's constant divided by 2π, m^* is the effective mass of the electrons in silicon, q is the electronic charge and E_{field} is the applied electric field across the film.

When an electron strikes the Ag-Si interface, it is only the energy component perpendicular to this boundary that is effective in transmitting the electron through the barrier. At a given energy E, this perpendicular component is a function of the angle θ between the **k** vector of the electron wave and the normal to the surface by [5]

$E\perp = E\cos^2\theta$. Since θ is not known for a given energy E, we used the volume average of $E\perp$ throughout the sphere, resulting in $E_{avg}\perp = E/3$. Equation (5) does not take into consideration the lowering of the barrier due to the field. This lowering is given by[8]

$$\Delta\phi = \sqrt{\frac{qE_{field}}{4\pi\varepsilon_{Silicon}}} \quad (6)$$

,

where $\varepsilon_{silicon}$ is the permittivity of silicon at room temperature ($12\varepsilon_o$). At each electric field $\Delta\phi$ was subtracted from the barrier height of 0.6eV.

Composite films of Ag/n-Si, 2µm thick, were deposited by magnetron co-sputtering on high resistivity ($\rho>10^3$ Ω-cm) 3-in. diameter Si (111) substrates, held at 400 ^{0}C. Preparation at this low temperature produces small Ag particles which have been shown to have higher photoelectronic sensitivities than larger ones[1]. The particles were equi-axed and mostly 5nm in size[9].We approximated them by spheres, in the usual effective medium approximation, when the incident wavelengths are much larger than the particle sizes[10]. From XRD measurements the silicon was found to be completely amorphous. 5nm was used in calculating the probabilities given in equations (2) and (3). Room temperature mean free paths for Ag at 3, 5, 8 and 14µm were taken from experimental data in B. Ziaja et al[11]. The measured absorption at these wavelengths gave fractions of incident radiation absorbed of 0.60, 0.45, 0.42 and 0.52 respectively[12]. The films contained 20 at% Ag and 80 at% Si as determined from Rutherford Backscattering Analyses. Thus, the system to which we applied equation (1), consisted of 2µm thick Ag/n-Si composite films, with 20 at% Ag having a uniform distribution of 5nm Ag particles. The silicon can be heavily doped with phosphorous ($\sim10^{19}/cm^3$) to produce a narrow depletion region at the Ag-Si interfaces and large electric fields in the depletion regions for increased tunneling[13], though such a model is unnecessary for the calculation of η(υ). The absorption coefficient was determined from the fraction of incident power remaining for transmission. At 14µm this fraction was 0.48 and is equal to exp(-αx). With x = 2µm, $\alpha = 3.67\text{x}10^3$ cm^{-1}. α for 3, 5 and 8µm may similarly be obtained. Spitzer and Fan[14] measured the room temperature absorption coefficient for free electrons in arsenic, antimony and phosphorus doped silicon over the wavelength range from 1 to 50µm. We interpolated their results to a phosphorus doping density of $10^{19}/cm^3$. The interpolated absorption coefficients at 3, 5, 8 and 14µms were 50, 75, 150 and 350 cm^{-1} respectively. For a 2µm thick film they corresponded to attenuated fractions of only 0.01, 0.02, 0.03 and 0.068 respectively, very small compared to the absorption in the Ag particles. These values were subtracted from the total attenuation to obtain the values for those due to the Ag particles, giving ή(υ) values of 0.59, 0.43, 0.39 and 0.45 at 3, 5, 8 and 14µm. An effective mass m^* of $0.3m_o$ was used in the calculation for η(υ) that is near the middle range of $(0.07 - 0.7)m_o$ of the published values for amorphous silicon[15]. η(υ) is plotted in Figure 2 below using the measured values for the absorbed radiation at the four wavelengths. Experiments are currently underway to validate these results in the Ag/n-Si system. It is to be noted that in the As precipitates in GaAs[3] where the fraction of radiation absorbed was 3%, the room temperature quantum efficiency was 2-2.5%, in good agreement with the results here. At an electric field of $2\text{x}10^6$ volts/cm, the quantum efficiency varies between 10 and 35% depending on the wavelength, which are quite large values for room temperature. The efficiency increases rapidly with electric field beyond this value and asymptotically approaches $\acute{\eta}(\upsilon)T(E_{avg}\perp)P_t(E)$ as $T(E_{avg}\perp)$ approaches unity. When both $T(E_{avg}\perp)$ and $P_t(E)$ are unity, the quantum efficiency $\eta(\upsilon)$, is equal to $\acute{\eta}(\upsilon)$, i.e., the absorbed radiation is completely converted into generating an electrical signal which would be expected under these conditions.

For operation as an infrared detector using a heavily doped model, some degree of cooling would be necessary, as for phosphorous doped silicon with a dopant density of 10^{19}/cm, there will be $2.2 \times 10^{18}/cm^3$ free electrons in the conduction band of silicon at room temperature that will contribute to the noise in such a device. As noted above the quantum efficiency is not a function of the doping density in the silicon, but mainly of the microstructure of the Ag/n-Si composite. This is an important distinction and will be examined in detail in future work where other models are discussed.

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Figure Captions

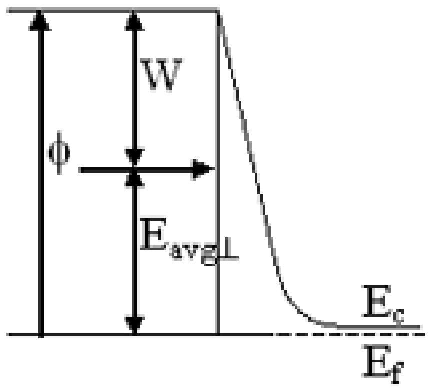

Figure 1. Energy band diagram at the Ag-Si interface. The horizontal axis represents the direction of the perpendicular component of the energy E.

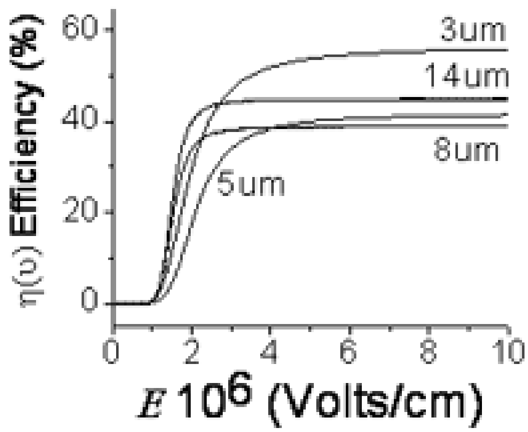

Figure 2. Quantum efficiency vs. electric field for 3,5,8 and 14μm incident wavelengths